

1 **Dissolved organic matter in newly formed sea ice and surface seawater**

2 Krista Longnecker

3 Woods Hole Oceanographic Institution, Marine Chemistry and Geochemistry, Woods Hole, MA

4 02543, U.S.A. klongnecker@whoi.edu

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12 **Abstract**

13 Changes in sea ice in the Arctic will have ramifications on regional and global carbon
14 cycling. Research to date has primarily focused on the regional impacts to biological activity and
15 global impacts on atmospheric processes. The current project considers the molecular-level
16 composition of organic carbon within sea ice compared to the organic matter in seawater. The
17 project revealed that the composition of organic matter within sea ice was more variable than the
18 composition of organic matter within the surface ocean. Furthermore, sea ice samples presented
19 two distinct patterns in the composition of organic matter with a portion of the sea ice samples
20 containing protein-like organic matter. Yet, the samples were collected in the early winter period
21 when little biological activity is expected. Thus, one hypothesis is that physical processes acting
22 during the formation of sea ice selectively transferred organic matter from seawater into sea ice.
23 The present project expands our understanding of dissolved organic matter in sea ice and surface
24 seawater and thereby increases our knowledge of carbon cycling in polar regions.

25 **1 Introduction**

26 Sea ice in the Arctic has recently experienced a dramatic decline in spatial extent
27 (Comiso et al., 2008; Kwok et al., 2009) which has ramifications for the entire Arctic ecosystem
28 (McLaughlin et al., 2011; Bhatt et al., 2014). While the loss of sea ice can impact the biological
29 community that relies on sea ice as a habitat (Arrigo, 2014), sea ice itself stores organic carbon
30 that can serve as a carbon and energy source for the base of the Arctic food web. Furthermore,
31 laboratory experiments (Müller et al., 2013) and field projects (Granskog et al., 2004; Stedmon et
32 al., 2007; Underwood et al., 2010) have shown that dissolved organic matter is not transferred
33 conservatively from the water column into sea ice during the formation of sea ice.

34 Dissolved organic matter in the Arctic region has several sources, including *in situ*
35 primary production, river input, and transport of seawater from adjacent oceans into the Arctic
36 (Wheeler et al., 1997; Anderson, 2002; Amon, 2004). Sinks for dissolved organic matter in the
37 Arctic include microbial remineralization of organic matter, settling based on association with
38 particles, outflow of surface waters into the north Atlantic Ocean, and deep-water formation in
39 the north Atlantic Ocean (Wheeler et al., 1997; Opsahl et al., 1999; Mathis et al., 2005). Within
40 sea ice, the dissolved organic matter is a combination of organic matter from the underlying
41 water column and *in situ* production by phytoplankton (Stedmon et al., 2011; Aslam et al., 2012).
42 As sea ice ages, the microbial community within sea ice uses the dissolved organic matter as a
43 carbon and energy source thereby altering the composition of the dissolved organic matter
44 (Stedmon et al., 2007). The present project focuses on newly formed sea ice in order to consider
45 conditions with minimal biological alteration of dissolved organic matter.

46 Previous characterizations of organic matter within sea ice have described broad classes
47 of organic compounds such as carbohydrates, amino acids, lipids, and extracellular
48 polysaccharides (EPS). Carbohydrate concentrations in sea ice are highly variable, with average
49 concentrations of up to 40% of the dissolved organic carbon in sea ice (Herborg et al., 2001;
50 Thomas et al., 2001; Dumont et al., 2009; Underwood et al., 2010). Amino acids have also been
51 measured within sea ice, although they are generally less than 8% of the organic carbon pool
52 (Arrigo et al., 1995; Amon et al., 2001; Dumont et al., 2009; Müller et al., 2013). The lipids in
53 sea ice originate from microbial biomass and their abiotic degradation can serve as a model for
54 the loss of organic matter within sea ice (Rontani et al., 2014). Finally, phytoplankton within sea

55 ice have been directly tied to the production of EPS within sea ice (Herborg et al., 2001; Meiners
56 et al., 2003; Riedel et al., 2006; Underwood et al., 2010; Underwood et al., 2013).

57 The EPS produced by phytoplankton is chemically complex (Ewert and Deming, 2013)
58 and can alter the physical structure of sea ice (Krembs et al., 2011). Yet, EPS is generally high
59 molecular weight organic material and thus represents only a fraction of the organic compounds
60 potentially present in sea ice.

61 Dissolved organic matter is a complex and heterogeneous mixture and no single
62 analytical method is capable of defining the composition of organic matter. In the present
63 project, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is applied to
64 assessing the molecular-level composition of low molecular weight organic matter. When used
65 in conjunction with electrospray ionization (ESI), the instrument is able to measure the mass-to-
66 charge values of thousands of organic compounds without fragmenting the compounds
67 (Kujawinski et al., 2002). The resulting data have an accuracy of less than 1 ppm which enables
68 the calculation of elemental formulas solely based on the mass-to-charge values (Kujawinski and
69 Behn, 2006; Koch et al., 2007). While structural isomers cannot be resolved with this
70 instrumentation, the resulting data provide valuable information on the molecular level
71 composition of organic matter from different ecosystems. FT-ICR MS has been used to define
72 marine and freshwater source molecules (Kujawinski et al., 2009) and to reveal patterns in the
73 dissolved organic matter found in terrestrial streams (Sleighter et al., 2014) and the marine
74 environment (Dittmar and Koch, 2006; Hertkorn et al., 2013). Thus far, the molecular level
75 composition of organic matter in sea ice is unknown, yet given the prospect for rapid changes in
76 the region, this represents a critical area for understanding carbon cycling in the Arctic.

77 Assessments of the organic matter in snow and glacial ecosystems provide the closest
78 approximations to the samples analyzed in the present project. In the northern hemisphere,
79 ultrahigh resolution mass spectrometry has been used to describe the biological imprint on the
80 composition of dissolved organic matter in glacial environments (Bhatia et al., 2010; Singer et
81 al., 2012; Lawson et al., 2014). In the southern hemisphere, analysis of Antarctic snow pack
82 revealed a terrestrial impact on the molecular-level composition of dissolved organic matter
83 (Antony et al., 2014). Furthermore, organic matter in glaciers can be the result of autochthonous
84 production (Bhatia et al., 2010; Singer et al., 2012) or atmospheric deposition of organic matter
85 onto the glacial surface (Jenk et al., 2006; Jurado et al., 2008; Stubbins et al., 2012). Ultimately,
86 these land-based glacial systems are a potentially important source of organic carbon to marine
87 ecosystems (Hood et al., 2015). However, whether the organic matter within sea ice follows the
88 same compositional patterns as terrestrial glacial ecosystems is unknown.

89 The present project considers organic matter within first year sea ice and seawater
90 samples from the underlying water column. The project used ultrahigh resolution mass
91 spectrometry to assess the composition of the dissolved organic compounds. The resulting data
92 provide baseline information on the dissolved organic matter in seawater and sea ice while
93 raising interesting questions about the sources of organic matter in sea ice.

94 **2 Materials and Methods**

95 **2.1 Sample collection**

96 Seawater and sea ice samples were collected in November and December of 2011 during
97 a cruise on board the USCGC *Healy*. At each station, one seawater and one sea ice sample were
98 collected. Surface water samples were collected with 30 L Niskin bottles. Sea ice samples were

99 collected with a dip net or were recovered on top of the CTD rosette system. The thickness of the
100 sea ice samples ranged from 8 to 15 cm (n=5); spatial variability in the thickness of the ice sheet
101 in the vicinity of the ship is unknown. Ice samples were melted in combusted glass beakers held
102 at room temperature in order to obtain water that could be processed with the solid phase
103 extraction protocol. Thus, the analyses described below are homogenized sea ice samples
104 because it was not possible to collect cores of sea ice nor was it possible to collect replicate
105 samples at each station. Both water and ice samples were sequentially filtered through GF/F
106 filters (Whatman) and 0.2 μm Omnipore filters (Millipore) in order to remove particulate organic
107 matter including any microbial cells within the samples. The filtered water samples were
108 acidified to pH \sim 3 with concentrated hydrochloric acid (HCl).

109 **2.2 Sample processing**

110 To obtain the concentration of total organic carbon (TOC), a 40 ml aliquot of whole
111 water was acidified to pH \sim 3 with concentrated HCl and stored in combusted glass vials at 4°C
112 until analysis with a Shimadzu TOC-V_{CSH} total organic carbon analyzer. Blanks (MilliQ water),
113 standard curves with potassium hydrogen phthalate, and comparisons to standards provided by
114 Prof. D. Hansell (University of Miami) were made daily. The coefficient of variability between
115 replicate injections was < 2 %. The concentration of dissolved organic carbon (DOC) was
116 obtained from 0.2 μm -filtered water using the same analytical method.

117 Dissolved organic matter (DOM) was extracted from 2 L of an acidified water sample
118 with 1g / 6 ml Bond Elut PPL cartridges (Varian) following the protocol from Dittmar et al.
119 (2008). After filtering the acidified water through the PPL cartridge, the cartridge was rinsed
120 with four cartridge volumes of 0.01 M HCl and the cartridge was dried. The DOM was eluted off

121 the cartridges using two cartridge volumes of 100% methanol and stored at -20°C. Due to
122 excessive salt content, samples were dried down on land and resuspended in an equivalent
123 volume of 5% methanol and 95% Milli-Q water which had been adjusted to pH~3 with
124 concentrated HCl. Samples were then re-extracted with 50mg/1ml PPL cartridges (Varian) and
125 the extracts were dried down until analysis by mass spectrometry.

126 **2.3 FT ICR MS data collection**

127 All samples were analyzed in negative ion mode on a 7T ESI FT-ICR mass spectrometer
128 (LTQ-FT-MS, Thermo Fisher Scientific, Waltham MA). Sample aliquots were reconstituted in
129 50:50 methanol:water and infused into the ESI interface at 4 $\mu\text{L min}^{-1}$. Instrument and spray
130 parameters were optimized for each sample. The capillary temperature was set at 250°C, and the
131 spray voltage was between 3.7 and 4 kV. At least 200 scans were collected for each sample
132 which is a sufficient number of scans for good peak reproducibility (Kido Soule et al., 2010).
133 The mass range for the full-scan collection was $150 < m/z < 1000$. Weekly mass calibrations
134 were performed with an external standard (Thermo Calibration Mix) resulting in mass accuracy
135 errors < 1.5 ppm. The target average resolving power was 400,000 at m/z 400 (where resolving
136 power is defined as $m/\Delta m_{50\%}$ where $\Delta m_{50\%}$ is the width at half-height of peak m).

137 **2.4 Peak Detection**

138 We collected individual transients as well as a combined raw file using xCalibur 2.0.
139 Transients were co-added and processed with custom-written MATLAB code provided by
140 Southam et al. (2007). Within each sample, only those transients whose total ion current (TIC)
141 was greater than 20% of the maximal TIC were co-added, processed with Hanning apodisation,
142 and zero-filled once prior to fast Fourier transformation. Mass-to-charge (m/z) values with a

143 signal-to-noise ratio above 5 (as calculated in Southam et al., 2007) were retained. Furthermore,
144 m/z values had to be present in at least two sea ice or two seawater samples. The impact of these
145 parameters can be seen visually in the van Krevelen diagrams in Fig. S1. Spectra were
146 internally re-calibrated using a short list of m/z values present in a majority of the samples. The
147 individual sample peak lists were then aligned with an error tolerance of 1 ppm using MATLAB
148 code provided by Mantini et al. (2007).

149 Elemental formulas were assigned using the Compound Identification Algorithm (CIA:
150 Kujawinski and Behn, 2006; Kujawinski et al., 2009) using a formula error of 1 ppm, and a
151 relationship error of 20 ppm. The mass limit above which elemental formulas were assigned only
152 by functional group relationships was 500 Da. Elements considered in CIA are C, H, O, N, S,
153 and P.

154 **2.5 Sea ice coverage**

155 The Climate Data Record of sea ice concentration from passive microwave data (Peng et
156 al., 2013) was used to characterize the extent of sea ice cover. The sea ice coverage is calculated
157 (in 25 x 25 km grid cells) from gridded brightness temperatures from the Defense Meteorological
158 Satellite Program (DMSP) F8, F11, and F13 Special Sensor Microwave Imager (SSM/I) passive
159 microwave radiometers and the DMSP F17 Special Sensor Microwave Image/Sounder (SSMS)
160 passive microwave radiometer. The netCDF files for each sampling day were downloaded from
161 the National Snow and Ice Data Center (Meier et al., 2013) and plotted using MATLAB.

162 **2.6 Statistical analysis**

163 Hierarchical cluster analysis was used to analyze inter-sample variability in ESI FT-ICR
164 MS data. For the cluster analysis, distances between samples were calculated with the relative

165 Bray-Curtis distance measure using the Fathom toolbox (Jones, 2014) in order to remove the
166 impact of differences in the number of m/z values in the sea ice compared to the seawater
167 samples. The cluster analysis was performed using Ward's linkage method (McCune and Grace,
168 2002). The Wilcoxon rank sum test and Kruskal-Wallis test were used to assess the significance
169 of differences across the samples. Post hoc tests after the Kruskal-Wallis test used a Bonferroni
170 correction for multiple comparisons. Variability in the number of m/z values and the proportion
171 of elemental formulas assigned within the sea ice and seawater samples was assessed by
172 calculating the coefficient of variation (CV) for each elemental formula, where the CV is defined
173 as the standard deviation divided by the mean value.

174 **3 Results**

175 **3.1 Environmental parameters**

176 The extent of sea ice cover increased as the sampling period progressed from mid-
177 November to early December (Fig. S2). Samples were collected both within the ice pack and at
178 the edge of the ice-water boundary. Surface water samples showed a small temperature
179 range, $-1.8\text{ }^{\circ}\text{C}$ to $-1.4\text{ }^{\circ}\text{C}$, and a slightly wider salinity range, 27.73 to a maximum value of 32.65
180 (Table 1). The salinity of the melted ice was 9.8 for the SLINE sample and 8.2 for the SLIE
181 sample. Salinity data are not available for the remaining sea ice samples. The concentrations of
182 DOC in the sea ice samples ranged from 31 – 109 μM , while values in the corresponding
183 seawater samples ranged from 60 – 85 μM (Table 1). In the seawater samples, most of the
184 organic matter was present as dissolved organic carbon with the average DOC/TOC ratio equal
185 to 1.02 (95% CI from 0.9029 to 1.1371). In the sea ice samples, DOC ranged from 35% to 100%
186 of total organic carbon (Fig. 1). For select samples, the concentrations of DOC exceeded the

187 TOC value due to the precision of the instrumentation used to obtain the organic carbon
188 concentrations (Sharp et al., 2002).

189 **3.2 Patterns in organic matter based on mass-to-charge values**

190 In order to characterize the organic matter in the sea ice and seawater samples, the
191 dissolved organic compounds have to be extracted from the water matrix. In this project, the
192 seawater samples showed higher extraction efficiencies than the sea ice samples (Table 2). We
193 tested the effect of pH on the extraction efficiency of the solid phase extraction cartridges (Fig.
194 S3) and found no significant difference between acidifying the fluids to pH=3 compared to pH=2
195 as described in the original method (Dittmar et al., 2008). The sea ice samples had significantly
196 lower numbers of m/z values compared to the seawater samples (Table 2, Wilcoxon rank sum
197 test, $p = 0.0011$). The decrease in the number of m/z values in the sea ice samples may be a
198 function of the decrease in DOC concentrations in the extract; however, reanalysis of the extracts
199 with differing DOC concentrations would be necessary to confirm this observation. Finally, the
200 CV calculated for the number of m/z features in the sea ice samples was higher than for the
201 seawater samples (36% in sea ice compared to 15% in seawater).

202 The patterns in the m/z values found in the sea ice and seawater samples were examined
203 using cluster analysis. This analysis does not require knowledge regarding the identity of each
204 m/z feature, instead the analysis relies on the pattern of shared m/z values among the samples in
205 the dataset. The sea ice and seawater samples formed distinct clusters suggesting a separation in
206 the composition of organic compounds between the two types of samples (Fig. 2). The cluster
207 analysis further revealed the sea ice samples were divided into two groups with three stations
208 (HS25, WN7, and PH9) distinct from the remaining sea ice samples. For simplicity, these

209 stations will be referred to as the ‘ice group #1 samples’ while the remaining sea ice samples will
210 be designated ‘ice group #2.’

211 A simple Venn diagram can be used to define the overlap in m/z values among the
212 seawater and two groups of sea ice samples (Fig. 3). Most of the m/z values in the ice group #2
213 samples were also present in the seawater indicating a high degree of overlap between the
214 organic matter in seawater and the organic matter in those ice samples. In contrast, most of the
215 m/z values obtained in ice group #1 were unique to ice group #1 and not found in either seawater
216 or the other sea ice samples.

217 **3.3 Composition of organic matter in sea ice and seawater**

218 Elemental formulas can be calculated for measured m/z values from ultrahigh resolution
219 mass spectrometry datasets. In the present project, elemental formulas were assigned to more
220 than 95% of the m/z values. CHO- and CHON-containing elemental formulas were the majority
221 of the formulas while CHONP, CHONS, and CHOS compounds represented a smaller
222 proportion of the calculated elemental formulas (Table 3, Table S1). Calculating the CV for each
223 group of elemental formulas revealed that the elemental formulas assigned to the sea ice samples
224 were more variable compared to those assigned to the seawater samples (Table 3). For example,
225 CHO compounds averaged 39% of the elemental formulas in the sea ice samples with a CV of
226 30% across the set of sea ice samples. In contrast, CHO compounds averaged 43% of the
227 seawater samples, but there was less variability with a CV of 7%. Magnitude-weighted averages
228 for the H:C and O:C molar ratios were also calculated for the m/z values with elemental formulas
229 (Table S3). The H:C_w and N:C_w values were significantly higher in the sea ice compared to the
230 seawater (Wilcoxon rank sum test, $p \ll 0.0001$ and $p = 0.0379$, respectively), while the O:C_w

231 values were significantly lower (Wilcoxon rank sum test, $p \ll 0.001$) in the sea ice compared to
232 the seawater.

233 van Krevelen diagrams (Fig. 4) are one means to display the chemical complexity of
234 organic matter (Kim et al., 2003). In a van Krevelen diagram, each point is an elemental formula
235 calculated from a measured m/z value. Fig. 4A is the elemental formulas observed in all of the
236 samples along with the formula classes that may be defined based on elemental ratios. The
237 regions defining protein-like compounds and condensed hydrocarbon-like compounds contain
238 the highest numbers of elemental formulas in both the sea ice and seawater samples (Table S2).
239 However, the distribution of elemental formulas was not uniform across the three sample groups.
240 The condensed hydrocarbon-like compounds (Fig. 5A) showed significant differences (Kruskal-
241 Wallis test, $p = 0.0246$), with a higher number of condensed hydrocarbon-like compounds in the
242 ice group #2 samples compared to the ice group #1 samples. There were also significant
243 differences in the number of protein-like compounds (Fig. 5B, Kruskal-Wallis test, $p = 0.0024$)
244 with the ice group #1 samples showing significantly more protein-like compounds than the water
245 samples. The remaining compound classes comprised less than 3% of the elemental formulas and
246 are therefore not considered further.

247 The difference between the ice group #1 and ice group #2 samples can also be viewed
248 graphically on the van Krevelen diagram (Fig. 4B). The m/z values common to all of the ice
249 group #1 samples have higher hydrogen:carbon molar ratios than the elemental formulas
250 calculated for the ice group #2 samples. In contrast, the ice group #2 had m/z values spanning a
251 broader range of molar ratios within the van Krevelen diagram.

252 **4 Discussion**

253 **4.1 Bulk characteristics of organic matter in sea ice and seawater**

254 In pelagic marine ecosystems, the majority of organic carbon in seawater is present in the
255 dissolved phase with a correspondingly low fraction of particulate organic carbon (Carlson et al.,
256 1998; Hansell and Carlson, 1998) which matches observations in the present project for the
257 seawater samples. In contrast, the sea ice samples had as little as 35% of the carbon present in
258 the dissolved form. The gradient in the fraction of carbon present as DOC is also notable with the
259 northern stations containing primarily DOC with decreasing fractions of DOC in the southern
260 stations. In land-fast ice collected from Barrow, Alaska, Juhl et al. (2011) measured DOC values
261 that were 66 to 80% of their TOC measurements. Dumont et al. (2009) obtained similar data with
262 DOC representing 77% of the TOC pool in sea ice collected from Antarctica. The change in the
263 fraction of carbon present as DOC could be salinity driven flocculation of organic carbon which
264 shifted organic matter from the dissolved phase to the particulate phase (Sholkovitz, 1976). This
265 process has been studied in estuaries where relatively fresh and saline waters mix and thereby
266 reduce the amount of DOC in the water column (Asmala et al., 2014). While the formation of sea
267 ice alters salinity, the consequences for the flocculation of organic matter is unknown. Based on
268 the data from the present project, the melting of sea ice in the northern regions would therefore
269 release a higher fraction of dissolved material to the water column compared to the southern
270 samples. This difference in the form of organic matter may affect the biological utilization of the
271 organic matter once it is released into the water column.

272 The current project assessed the composition of dissolved organic matter and relied on
273 solid phase extraction to extract organic compounds from seawater and sea ice. Yet, the

274 extraction of organic matter from water samples is not 100% efficient and is partially dependent
275 on the organic compounds within the samples. For samples from marine and estuarine sites,
276 Dittmar et al. (2008) reported extraction efficiencies ranging from 43 to 62% using the PPL
277 extraction cartridges. More recently, a series of seawater samples had extraction efficiencies
278 ~40% (Arrieta et al., 2015) which is comparable to the extraction efficiencies measured in the
279 Arctic seawater samples. In contrast, the extraction of organic carbon from sea ice was more
280 variable with extraction efficiencies ranging from 9 to 34%. Using C₁₈ extraction disks, Bhatia et
281 al. (2010) observed an even larger range of extraction efficiencies from glacial samples (5 –
282 94%) suggesting that some of the variability observed in the sea ice may be a function of organic
283 matter found within ice samples. Since the analysis of organic matter in these samples required
284 solid phase extraction, the conclusions are biased towards the extractable organic matter and may
285 not represent the larger pool of organic matter in sea ice or seawater.

286 **4.2 Composition of DOM in sea ice compared to marine systems**

287 Direct comparison of ultrahigh resolution mass spectrometry data across research sites is
288 complicated by the use of different mass spectrometers and different computational algorithms
289 used to process the data and generate the elemental formulas. However, some broad comparisons
290 are possible. The prevalence of m/z values with CHO and CHON containing formulas in the sea
291 ice samples is comparable to samples from the Greenland ice sheet (Lawson et al., 2014) and in
292 snow from the Antarctic (Antony et al., 2014). Thus, the distribution of elemental formulas is
293 similar, although converting the percent of elemental formulas containing N, for example, into
294 the concentration of N-containing organic matter is not possible with this type of ultrahigh
295 resolution mass spectrometry data. The magnitude-averaged elemental ratios of H:C and O:C

296 observed for the sea ice samples in the present project also span the range of magnitude-averaged
297 elemental ratios measured on the Greenland ice sheet (Bhatia et al., 2010; Lawson et al., 2014).
298 On the other hand, the Arctic seawater samples have a higher proportion of CHON compounds
299 compared to values obtained from more temperate oceans (Kujawinski et al., 2009). Lacking any
300 other Arctic seawater samples for comparison, we cannot assess whether these patterns are
301 unique to polar regions or is a function of the organic matter present in seawater samples during
302 the polar winter.

303 **4.3 Selective transfer of organic compounds into sea ice**

304 The formation of sea ice is a dynamic process. This project focused on newly formed sea
305 ice in order to reduce the impact of primary production and alteration of organic matter within
306 the sea ice due to biotic processes. Yet, even in the fall to winter transition, there could be a low
307 rate of biological activity within the sea ice with an unknown impact on the organic matter. For a
308 subset of the sea ice samples, the total organic carbon concentration of the sea ice exceeded the
309 value for the seawater. The source of this organic carbon could be primary production within the
310 ice or atmospheric deposition. Alternatively, the sea ice could have been formed at a site with
311 higher concentrations of organic carbon in the water column and subsequently transported to the
312 location where the ice was sampled. Bulk assessments of sea ice have revealed the formation of
313 sea ice differentially enriches dissolved organic matter (Thomas et al., 2001) in a manner that
314 does not match the enrichment of inorganic compounds within sea ice (Giannelli et al., 2001).
315 Here, ultrahigh resolution mass spectrometry data provides new insight into how variability in
316 the composition of organic matter affects whether a compound is assimilated into sea ice. First,
317 the data revealed clear distinction between the composition of organic matter in seawater and sea

318 ice indicating that seawater samples cannot serve as a proxy for the organic matter that may be
319 trapped within sea ice. Yet, the sea ice further divided into two groups each with a different level
320 of overlap with seawater. The m/z values within ice group #2 were predominantly m/z values
321 found in seawater. In contrast, the m/z values within ice group #1 were more distinct from
322 seawater with a particular overrepresentation of protein-like compounds.

323 The current project is not the first to observe protein-like material within sea ice.
324 Stedmon et al. (2011) used fluorescence measurements to identify protein-like material as one
325 pool of compounds within sea ice dissolved organic matter. Their samples were collected in the
326 winter to spring transition and they conclude that *in situ* production is the driving factor defining
327 the presence of proteins in sea ice (Stedmon et al., 2011). On the other hand, amino acids show
328 enrichment in sea ice compared to seawater (Müller et al., 2013), which implicates selective
329 assimilation as an important factor dictating the composition of organic compounds found within
330 sea ice. In the Arctic, the fall to winter transition is a period of low biological activity, thus our
331 observation of enrichment of protein-like material within the ice group #1 samples is likely due
332 to physical processes and not *in situ* production within the sea ice.

333 The available data could not explain why there were two types of sea ice samples in the
334 present project. All three of the stations within ice group #1 samples were from the Beaufort and
335 Chukchi Seas. Yet, even stations that were relatively close (HS25 and BC6, or PH9 and PH3, see
336 Fig. 1) showed different patterns in the composition of organic matter. This suggests that spatial
337 proximity and the movement of surface water currents in the region cannot explain the
338 differences. The conditions in the surface ocean with respect to DOC and TOC concentrations,
339 the abundance of heterotrophic and autotrophic microorganisms, nutrient concentrations, and

340 surface water temperature (data not shown) also could not explain the distinction between the
341 two groups of ice samples.

342 The presence of two groups of sea ice samples also contributed to the increased
343 variability in the organic matter in sea ice compared to seawater. The bulk assessments of the
344 concentration of TOC and DOC in the sea ice and the chemical complexity of the dissolved
345 organic matter in sea ice spanned a larger range than was observed in the seawater samples.
346 Organic matter in sea ice is spatially heterogeneous (Underwood et al., 2010; Juhl et al., 2011)
347 and the current project's data emphasizes that the heterogeneity of sea ice extends to
348 compositional differences in the organic matter. FT-ICR MS data cannot be used to assess
349 structural isomers in the organic compounds. However, we posit that within a single m/z value,
350 the sea ice samples would also have more structural isomers compared to what would be present
351 in the seawater samples. Furthermore, this complexity of organic compounds in sea ice indicates
352 that small sets of sea ice samples may not be representative of processes occurring across the
353 Arctic region which hinders our ability to predict the role of changes in sea ice on polar
354 ecosystems.

355 **5 Conclusions**

356 Future changes in the spatial extent and thickness of sea ice will directly impact polar
357 ecosystems. Reductions in sea ice will also transfer organic matter into the water column. One
358 goal of this project was to assess the potential resemblance between this sea ice-derived organic
359 matter and the organic matter already present in seawater. While the organic matter in sea ice
360 was distinct from that in seawater, it was not uniformly different which complicates linking
361 future changes in sea ice with carbon cycling in polar regions. The current project has provided

362 baseline information about the composition of organic matter in sea ice. Future research must
363 address the factors that control the transfer of individual organic compounds between the water
364 column and sea ice and consider regional variability in these processes. Ultimately,
365 compositional differences in organic matter directly impacts its availability to the biological
366 community and thus controls the movement of carbon through the Arctic ecosystem.

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547 dissolved organic carbon. *Deep-Sea Res II* **44**, 1571-1592.

548

549

550 Table 1. Paired sea ice and seawater samples were collected from eight stations in the Bering, Beaufort, and Chukchi Seas. Total
 551 organic carbon (TOC) and dissolved organic carbon (DOC) concentrations are given for the ice and seawater samples. For the
 552 seawater samples, additional details include sampling depth, temperature, and salinity of the water.

Station	Date sampled (GMT)	Latitude (°N)	Longitude (°W)	Water samples					Ice samples	
				Sample depth (m)	Temperature (°C)	Salinity	TOC (µM)	DOC (µM)	TOC (µM)	DOC (µM)
SLIE	Dec. 1, 2011	63.5	167.8	2.0	-1.6	31.68	72.3	74.9	109.2	37.4
SLINE	Dec. 2, 2011	64.6	168.5	2.0	-1.8	32.65	63.6	60.1	101.4	55.9
PH9	Nov. 27, 2011	68.6	168.7	1.3	-1.4	32.03	66.4	65.3	68.1	38.1
PH3	Nov. 28, 2011	68.6	167.3	5.2	-1.6	31.74	85.1	84.3	39.5	38.6
WN7	Nov. 17, 2011	71.3	161.3	2.5	-1.6	31.88	74.5	78.3	99.2	102.4
BC6	Nov. 21, 2011	72.1	155.3	1.2	-1.6	29.67	69.3	74.4	48.8	47.1
HS17	Nov. 18, 2011	72.2	158	2.6	-1.7	31.66	74.3	73.0	46.5	46.5
HS25	Nov. 20, 2011	72.6	156	2.8	-1.5	27.73	69.6	72.1	31.8	31.2

553

554

555 Table 2. Extraction efficiency and the number of m/z values from the mass spectrometry data for
 556 the organic matter extracted from seawater and sea ice. The extraction efficiency is calculated as
 557 the percentage of dissolved organic carbon captured by the PPL cartridges as a fraction of the
 558 measured dissolved organic carbon in the corresponding water sample. The number of m/z values
 559 is the number of peaks detected in the FT-ICR MS data.

Station	Extraction efficiency (%)		# m/z values	
	Seawater	Sea ice	Seawater	Sea ice
SLIE	41	28	7760	4333
SLINE	38	10	7302	2975
PH9	33	17	7459	2539
PH3	32	22	5143	4673
WN7	34	9	5674	2637
BC6	43	22	7609	6588
HS17	42	17	7296	3654
HS25	39	34	7286	2665

560

561

562 Table 3. Elemental formulas were assigned to the measured m/z values from the dataset. The
 563 table shows the average percent of elemental formulas assigned to CHO, CHON, CHONP,
 564 CHONS, and CHOS groups in the seawater and sea ice samples from the present project. Table
 565 S1 provides the numbers for the individual samples. The values in the table are the averages for
 566 the full set of sea ice samples and for the ice group #1 and ice group #2 samples. The values in
 567 parentheses are the coefficient of variation (CV) for each group of elemental formulas.

568

	Mean percent (and CV) of elemental formulas			
	seawater	sea ice	ice group #1	ice group #2
CHO	43 (7%)	39 (30%)	34 (33%)	42 (29%)
CHON	30 (5%)	39 (33%)	50 (20%)	32 (33%)
CHONP	19 (5%)	13 (21%)	11 (7%)	15 (18%)
CHONS	2 (21%)	2 (41%)	1 (39%)	1 (28%)
CHOS	4 (8%)	4 (52%)	2 (31%)	5 (22%)

569

570 **Figure legends**

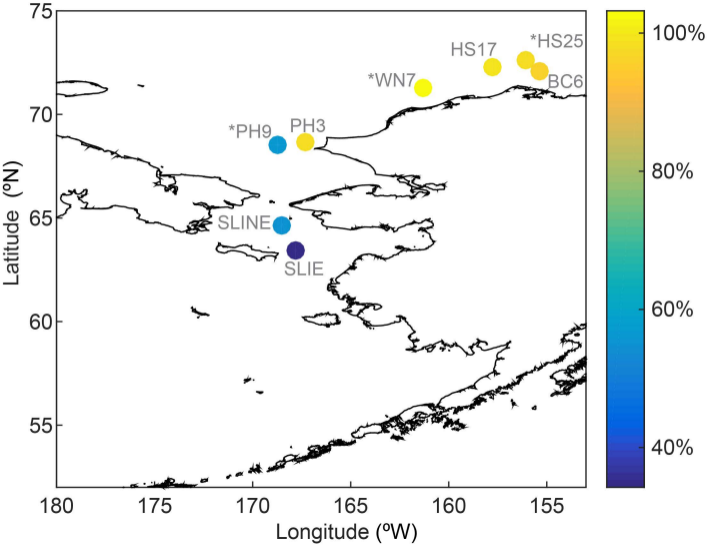
571 Fig. 1. Paired sea ice and seawater samples were collected from eight stations in the Bering,
572 Beaufort, and Chukchi Seas. The color bar shows the percent of total organic carbon in the sea
573 ice samples that is present as dissolved organic carbon (DOC divided by TOC, times 100). For
574 the seawater samples, this value was close to 100% for all of the samples (data not plotted). The
575 three stations marked with * are the ice group #1 stations discussed in the text.

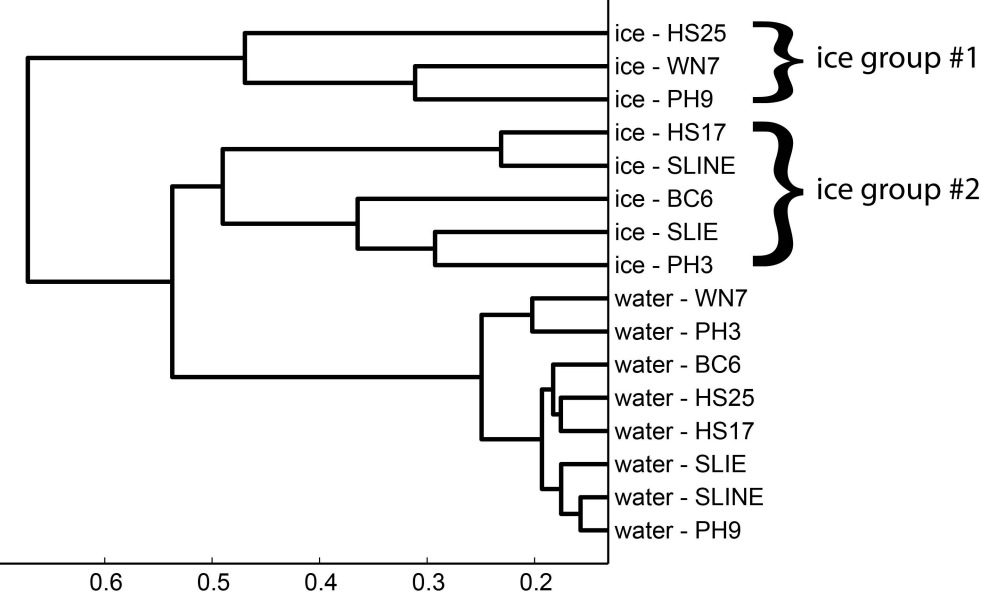
576 Fig. 2. Cluster analysis based on Bray-Curtis distance measures calculated for the ultrahigh
577 resolution mass spectrometry data obtained for organic matter from sea ice and seawater. The sea
578 ice samples clustered into two distinct groups: 'ice group #1' and 'ice group #2'.

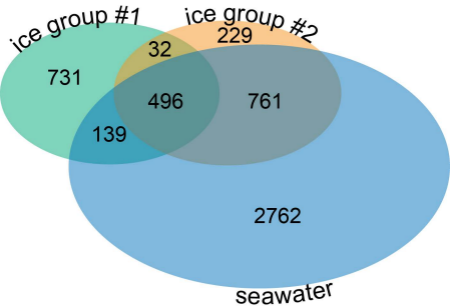
579 Fig. 3. Three-way Venn diagram showing the overlap in m/z values observed in the negative ion
580 mode data. The numbers within the diagram are the number of m/z values unique to each subset
581 of samples.

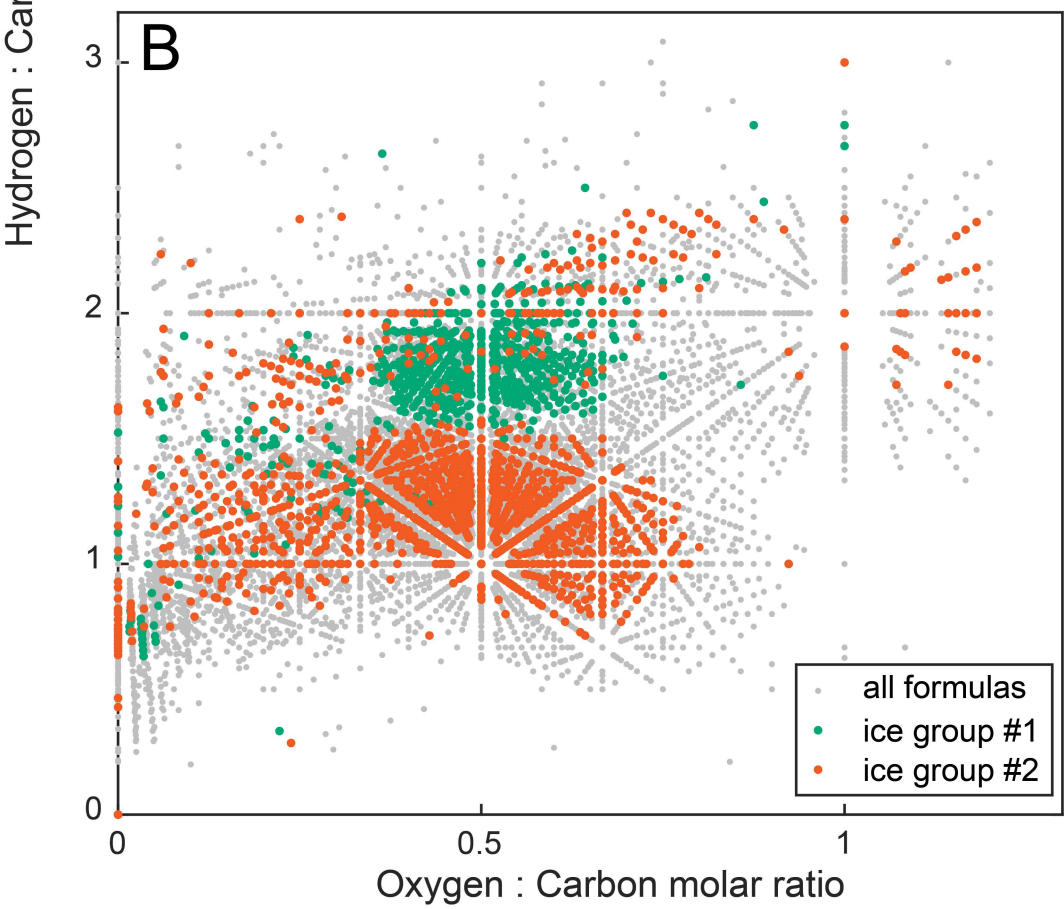
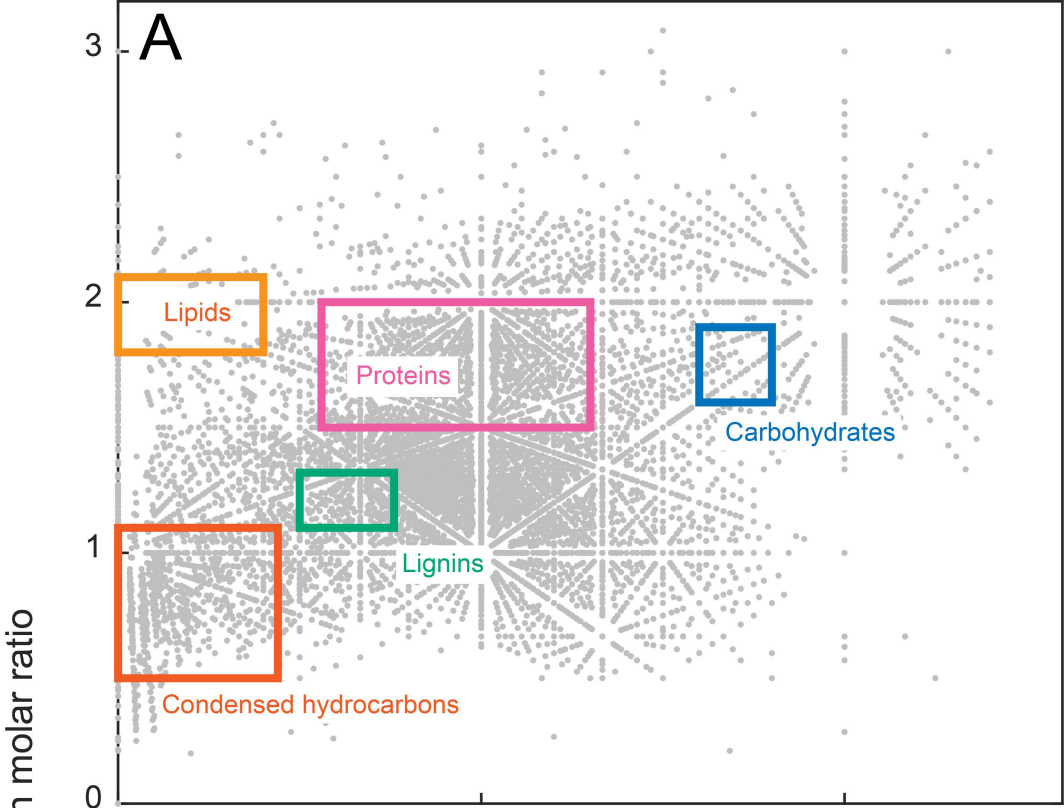
582 Fig. 4. van Krevelen diagrams plotting the oxygen:carbon and hydrogen:carbon molar ratios of
583 the elemental formulas in the seawater and ice samples. The complete set of elemental formulas
584 is given in gray. (A) Shows the compound classes that may be defined based on the O:C and H:C
585 molar ratios for the elemental formulas, while (B) shows the elemental formulas in the ice group
586 #1 and ice group #2 samples.

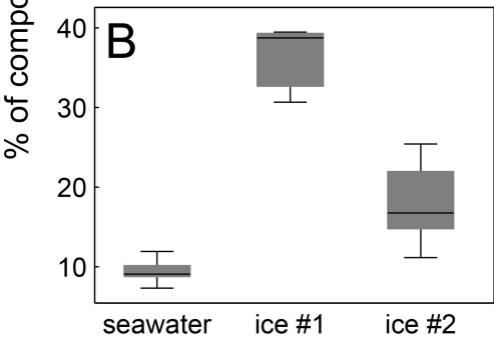
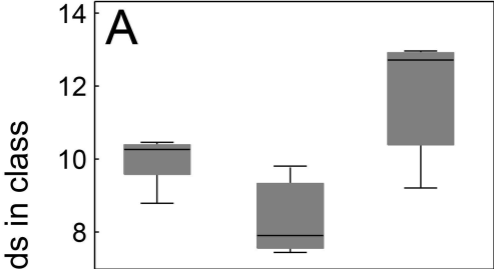
587 Fig. 5. Distribution of (A) condensed hydrocarbon-like compounds and (B) protein-like
588 compounds in the seawater samples, the ice group #1 samples, and the ice group #2 samples. The
589 data are given as the percentage of each group as fraction of the total number of m/z values
590 obtained from the samples. Table S2 shows the values for the individual samples.











Dissolved organic matter in newly formed sea ice and surface seawater

Krista Longnecker

Woods Hole Oceanographic Institution, Marine Chemistry and Geochemistry, Woods Hole, MA

02543, U.S.A. klongnecker@whoi.edu

Running title: DOM in the Arctic

Supplemental Information

Table S1. Elemental formulas were assigned to the measured m/z values. The table provides the number of elemental formulas within each group (CHO-, CHON-, CHONP-, CHONS-, and CHOS-containing formulas) for the seawater (upper portion of table) and sea ice (lower portion of table) samples. Table 3 provides the average values for the seawater and sea ice samples.

Station	CHO	CHON	CHONP	CHONS	CHOS
<i>Water</i>					
SLIE	3170	2416	1472	149	349
SLINE	2881	2266	1471	155	315
PH9	2974	2301	1502	147	329
PH3	2486	1362	940	56	192
WN7	2591	1638	994	78	222
BC6	3146	2283	1528	126	295
HS17	3122	2141	1376	126	300
HS25	3150	2160	1398	100	261
<i>Ice</i>					
SLIE	1748	550	422	15	113
SLINE	1326	1959	477	45	243
PH9	1104	999	302	19	31
PH3	1556	1830	674	41	265
WN7	919	1251	269	36	35
BC6	2309	2315	1227	67	347
HS17	1838	921	523	24	129
HS25	570	1542	281	46	55

Table S2. Elemental formulas can be characterized into compound classes based on elemental ratios. The classes can be visualized within the van Krevelen diagrams as shown in Figure 4. This table lists the number of elemental formulas in each class for the water samples (upper part of table) and the ice samples (lower part of table).

Station	Condensed hydrocarbons	Proteins	Lignins	Carbohydrates	Lipids
<i>Water</i>					
SLIE	716	721	196	77	3
SLINE	741	646	200	69	3
PH9	746	635	194	73	2
PH3	438	382	140	44	0
WN7	534	499	158	44	2
BC6	766	824	206	59	4
HS17	737	681	201	70	3
HS25	720	874	211	50	4
<i>Ice</i>					
SLIE	518	1098	60	22	66
SLINE	275	324	109	9	16
PH9	197	792	77	6	9
PH3	600	965	96	14	67
WN7	186	1018	62	1	9
BC6	830	1125	159	36	45
HS17	408	566	113	10	30
HS25	213	1095	47	1	20

Table S3. Elemental ratios were calculated as magnitude-averaged values from m/z values from the seawater (upper portion of table) and sea ice (lower portion of table) samples.

Station	H:C_w	O:C_w	N:C_w
<i>Water</i>			
SLIE	1.2	0.5	0.1
SLINE	1.2	0.5	0.1
PH9	1.2	0.5	0.1
PH3	1.2	0.5	0.1
WN7	1.2	0.5	0.1
BC6	1.2	0.5	0.1
HS17	1.2	0.5	0.1
HS25	1.2	0.5	0.1
<i>Ice</i>			
SLIE	1.5	0.4	0.2
SLINE	1.3	0.5	0.1
PH9	1.4	0.4	0.1
PH3	1.4	0.4	0.2
WN7	1.4	0.4	0.2
BC6	1.3	0.4	0.2
HS17	1.3	0.4	0.1
HS25	1.6	0.4	0.3

Figure S1. The figure shows the decreasing number of elemental formulas as the signal:noise ratio increases from 3, to 5, to 10. The subpanels on the right further restrict the m/z features by requiring a feature to be present in either two seawater or two sea ice samples. The colorbar indicates the number of samples containing each elemental formula; a total of 16 samples were analyzed in the current project. The final analysis was conducted with a signal:noise ratio of 5 and required each m/z value to be present in at least two seawater or two sea ice samples.

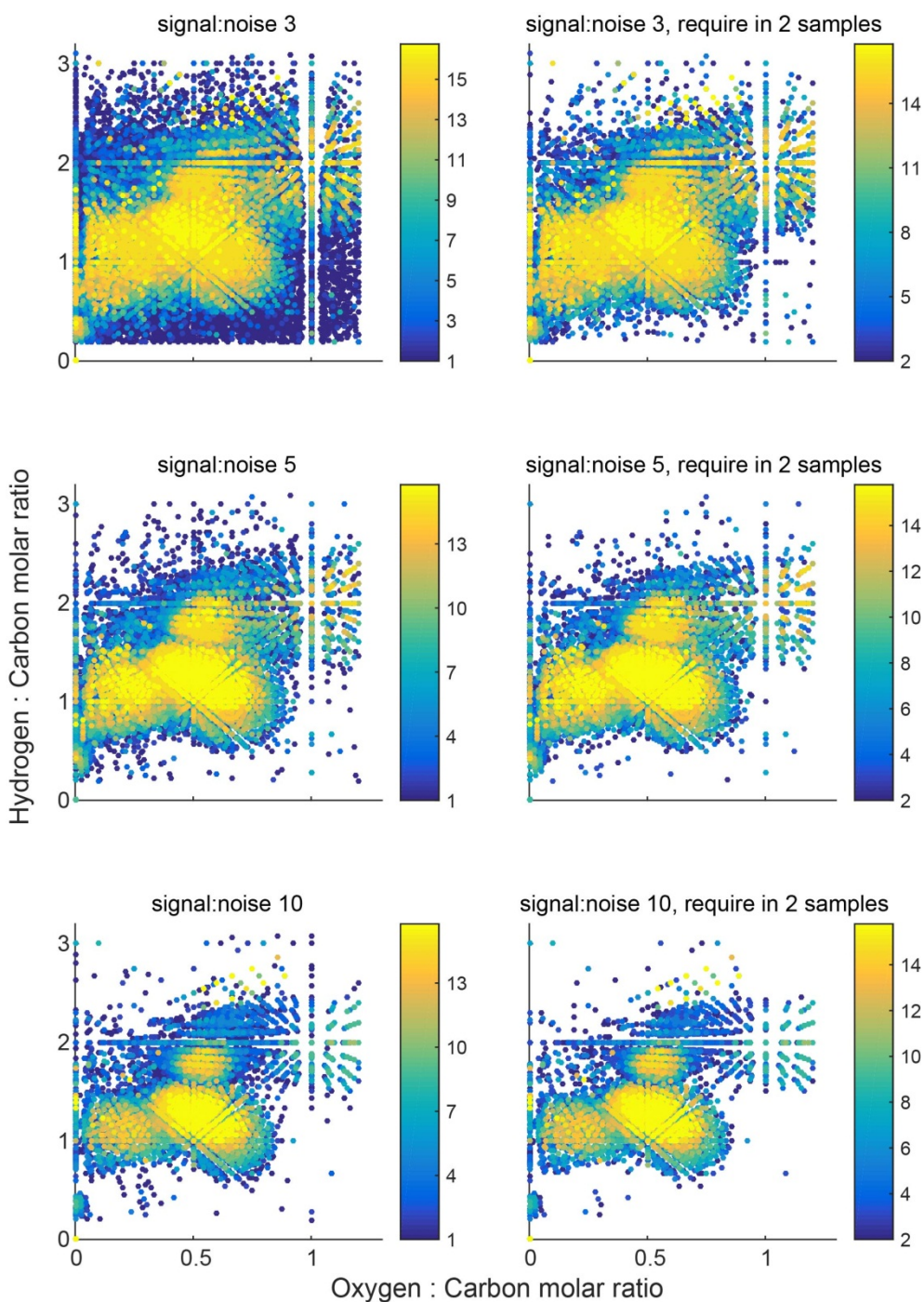


Figure S2. The sea ice cover from passive microwave data plotted for each sampling day. The color bar shows the percentage of sea ice cover. The pink circle is the geographic location for the corresponding day's sample collection.

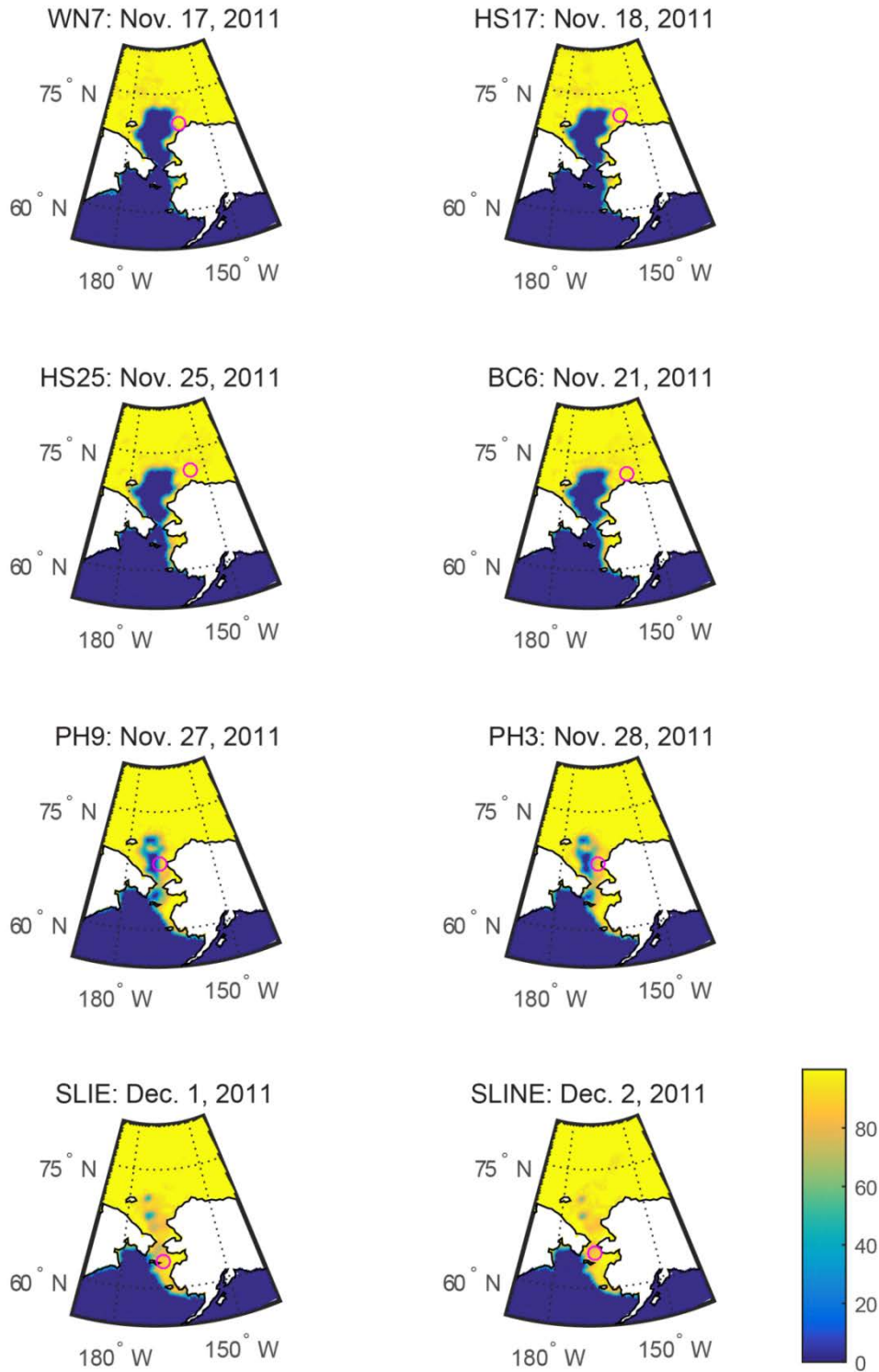


Figure S3. Vineyard Sound seawater was filtered through a 0.2 μm Omnipore filter and separated into three aliquots which were acidified to pH=2, pH=3, or pH=4 using 12 M HCl. The DOC from three, 100 ml aliquots of each treatment was extracted using PPL solid phase extraction cartridges. The initial DOC concentration of the seawater and the DOC concentration of the extracts were measured using a Shimadzu TOC- V_{CSH} total organic carbon analyzer. The figure shows the extraction efficiency of each replicate at the three different pH levels. While there was no significant difference in extraction efficiency at each pH level (one-way ANOVA, $F(2,6) = 1.81$, p -value 0.2), there was more variability in the extraction efficiency in the pH=4 treatment.

